A Convenient Catalytic Method for the Dihydroxylation of Alkenes by Hydrogen Peroxide

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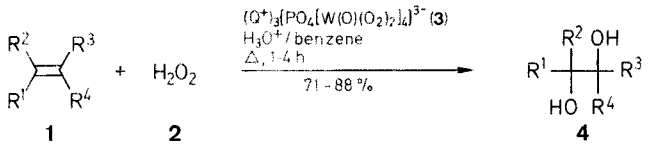
A simple method for preparing water-soluble *vicinal* diols from the corresponding water-insoluble alkenes is reported. It is based on the use of tungsten peroxo complexes as catalysts and hydrogen peroxide as the oxidizing agent in a two-phase system.

The dihydroxylation of alkenes to give *vic*-diols is a well-known and important reaction.[1] Among the existing methods for effecting this transformation,[2-5] the direct addition of hydrogen peroxide to olefinic compounds catalyzed by tungstic acid[5] is quite attractive. This method has the advantage of avoiding the use of expensive, toxic, and/or hazardous reagents or catalysts, of low consumption of chemicals, and of an easy work-up. However, it suffers from the inconvenience of being effective only, with a few exceptions,[6] when water-soluble olefinic compounds are used.

During our studies on selective oxidative processes with hydrogen peroxide catalyzed by the tungstate-phosphate ion association,[7-8] we had succeeded in discovering a new family of tungsten peroxo complexes, namely, quaternary ammonium tetrakis(diperoxotungsto)phosphates(3-) **3**, which were found to display high epoxidizing ability toward unactivated olefins, 1-alkenes included.[9] In particular, complexes **3a** and **3b** proved to be remarkably effective catalysts for this reaction when used together with 15% hydrogen peroxide solution in a two-phase system, and thus rendered possible the development of a new efficient and versatile epoxidation method.[10] We further observed that the activity of catalysts **3a** and **3b** may be maintained to a satisfactory degree even in more dilute hydrogen peroxide than that previously used by making the water phase of the two-phase system considerably more acidic (by addition of sulfuric acid) than that of the original system (pH 2.3); this presumably reduces hydrolysis of the peroxo heteropoly anion of the catalyst complex.[10] However, under these conditions, rather acid-sensitive epoxides such as those related to water-soluble *vic*-alkanediols were transformed into the diols. Utilizing these facts we have developed a simple and convenient one-pot procedure for the preparation of water-soluble *vic*-diols **4** from the water-insoluble olefins **1** via epoxidation-hydrolysis.



1 2 4

3a: $Q^+ = (n\text{-}C_8H_{17})_3\overset{+}{N}Me$
b: $Q^+ = [n\text{-}C_{18}H_{37}(76\%) + n\text{-}C_{16}H_{33}(24\%)]_2\overset{+}{N}Me_2$

1, 4	R^1	R^2	R^3	R^4
a	Ph	CH_3	H	H
b	H	H	H	CH_2Cl
c	H	H	CH_3	CH_2Cl
d	Ph	H	H	H
e	n-C_4H_9	H	H	H
f	H	$(CH_2)_3$		H
g	H	$(CH_2)_4$		H
h	H	$(CH_2)_5$		H
i	C_2H_5	H	C_2H_5	H
j	CH_3	CH_3	CH_3	CH_3

Table. *vic*-Diols **4** Prepared

Entry	Product	Amounts (mmol) used[a]			Reaction Conditions		30% H_2SO_4 added[b] (mL)	Eluent (mL)	Yield[c] (%)	mp (°C) (solvent) or bp (°C)/Torr	
		1	**3a**	**(3b)**	Temperature (°C), Time (min)	pH				found	reported
1	**4a**	260[d]	0.8	(0.6)	60, 75	1.5	4	Et_2O (500)	83 (84)	43–44 (Et_2O/pentane, 1:2, at −25°C)	43–44[20]
2	**4b**	260	0.8		reflux, 240	1.2	2	Et_2O (650)	74	83/2	116/11[21]
3	**4c**	260	0.8		reflux, 210	1.2	2	Et_2O (400)	71	75/2	114–117/20[22]
4	**4d**	260[d]	0.8	(0.6)	60, 75	1.5	4	Et_2O[e] (750)	82 (81)	65–66 (Et_2O/hexane, 1:1)	65–66[23]
5	**4e**	200[d]	0.8		reflux, 210	1.2	–[f]	Et_2O (900)	80	97–98/5	100/5[24]
6	**4f** (*trans*)	200	0.6		reflux, 120	1.5	4	Et_2O[e] (1500)	88	49–50[g]	48–49.5[25]
7	**4g** (*trans*)	150	0.4	(0.4)	70, 60	1.5	4	acetone[h] (300)	86 (87)	104–105 (benzene)	104.5–105.5[26]
8	**4h** (*trans*)	200	0.6		60, 120	1.5	4[f]	Et_2O[e] (650)	78	61–62 (toluene)	63[27]
9	**4i** (*meso*)	150[d]	0.6		reflux, 120	1.5	4	Et_2O[e] (600)	83	90–90.5 (hexane)	90–90.5[28]
10	**4j**	150	0.4		reflux, 75	1.5	4	–[i]	72	46–48 (H_2O)	46–47[29]

[a] Per 100 mmol of **2**, dissolved in H_2O [160 mL (entries 1–5,9) or 80 mL (entries 6–8,10)]. In entries 1, 4, and 7, either **3a** or **3b** was used.

[b] At the end of the reaction, to achieve satisfactory phase separation.

[c] Yield of isolated product, based on **2**; purity: ≥97% (GLC). All products gave satisfactory microanalyses: C ±0.25, H ±0.19, Cl −0.5.

[d] Reaction carried out without solvent.

[e] Et_2O/acetone, 4:1 (50 mL) (entries 4, 8) or 5:1 (30 mL) (entry 6), or 3:2 (60 mL) (entry 9) instead of Et_2O is used to dissolve the crude product.

[f] After phase separation, the organic layer is extracted with 1% H_2SO_4 (2 × 70 mL), and the extract is added to the aqueous layer.

[g] Highly hygroscopic product. Obtained as an oil which solidifies after distillation; bp 98°C/2 Torr (Lit.[25] bp 126.5–127.5°C/12 Torr).

[h] The acetone extract (brought to 250 mL with more acetone) is eluted as such. The purified product is further freed from small amounts of a colorless solid contamination by dissolution in boiling Et_2O (800 mL), filtration, and evaporation. A similar contaminant was found to accompany the crude product also in the other cases. However, it was removed during purification of the product on the column.

[i] Product isolated by crystallization from the aqueous layer.

In spite of the growing interest in Mo- or W-based heteropoly acid quaternary ammonium salt/hydrogen peroxide systems for the epoxidation of alkenes under two-phase conditions,[11,12] only one example to our knowledge has hitherto been reported concerning the direct hydroxylation of olefins via epoxides by such oxidizing systems.[13] The hydroxylation procedure used 30% hydrogen peroxide and tetraalkylammonium heteropoly-11-tungstates, but it was not selective owing to the formation of large amounts (30–45%) of oxidative cleavage products of the formed diol. The inconveniences hitherto connected with the use of such oxidizing systems in the olefin → diol transformation may be attributed to the usual epoxidation conditions [water phase very limited in volume (30–35% H_2O_2)], as we could ascertain experimentally. Under these conditions, we observed a substantial decrease (20 to 40%) in yield of diol owing to incomplete ring cleavage of the intermediate epoxide and/or to increased formation of by-products, which probably is due to the presence of the diol mainly in the organic phase. These inconveniences are overcome by the present procedure which is rendered possible by the high efficiency of the catalysts.

Our procedure uses very dilute (2–4%) hydrogen peroxide (**2**) as the primary oxidant and the above-mentioned methyltrioctylammonium and dimethyl[dioctadecyl(76%) + hexadecyl(24%)]ammonium tetrakis(diperoxotungsto)phosphates (**3a** and **3b**) as catalysts in an aqueous/organic two-phase system. It can be used for the dihydroxylation of 1-alkenes, non-terminal open-chain alkenes, and cycloalkenes in high yields under mild conditions, with reaction times of 1–4 hours. The large relative volume of the aqueous phase eliminates the need for separation of the product from the starting material, the formed diol being nearly quantitatively present in the water phase, from which it can be easily isolated.

The catalyst complexes **3a** and **3b** are prepared from tungstic acid, phosphoric acid, hydrogen peroxide, and the commercially available methyltrioctylammonium chloride or dimethyl[dioctadecyl(76%) + dihexadecyl(24%)]ammonium chloride (Arquad 2HT), respectively, according to the previously reported procedure.[10]

The dihydroxylation is performed at 60–70°C in a two-phase mixture of acidified (pH 1.2–1.5) aqueous hydrogen peroxide (**2**) and a benzene solution of the alkene **1** (molecular ratio **1**:**2** = 1.5–2.6:1) containing catalyst **3a** or **3b**. When the oxidant **2** has been almost completely consumed (1–4 h, iodometric titration) conventional work-up of the water phase affords diols **4** in good yield and purity (Table). The excess of alkene **1** required to obtain optimum yields of diol **4** depends on the reactivity of the alkene and also on the amount of catalyst used. The excess alkene is substantially unchanged after the reaction.

When the alkene is a liquid, the reaction may also be run without solvent. This variation was employed to advantage when a large excess of alkene was used or diol solubility in water was somewhat low (Table, entries 1, 4, 5); transfer of the diol into the water phase is thus favored.

As illustrated by entries 6–9 in the Table, the method effects *trans*-hydroxylation.

Water-soluble *vic*-diols are widely used for the synthesis of commercial products such as phenylacetaldehyde[14] and 2-phenylethanol,[15] as intermediates in the perfume and fragrance industry,[16] and for the manufacture of cosmetics,[17] polymers,[18] and photographic materials.[19]

All *vic*-diols **4** prepared are known. Their identity was confirmed by microanalyses, spectral data, and comparison with authentic samples. All alkenes **1** used were obtained commercially. Catalyst complexes **3a** and **3b** were prepared according to the reported procedure.[10] The pH measurements were performed using a Metrohom (E 532) digital-pH-meter. Melting points were determined by the Kofler method and are uncorrected. GLC analyses were performed on a Varian 3700 instrument equipped with a 25 m × 0.32 mm (i.d.) fused silica capillary column with CP-Sil 5 CB as stationary phase (0.15 μm film) (Chrompack), with column temperature programming.

3-Chloro-1,2-propanediol (4b); Typical Procedure (for 4a–i):

To a solution of H_2O_2 (**2**; 100 mmol) in H_2O (160 mL) (adjusted to pH 1.2 with 30% H_2SO_4) in a 500-mL round-bottomed flask fitted with stirrer, thermometer, and reflux condenser are added allyl chloride (**1b**; 19.9 g, 260 mmol), benzene (10 mL), and methyltrioctylammonium tetrakis(diperoxotungsto)phosphate (**3a**; 1.804 g, 0.8 mmol). The resultant two-phase mixture is heated to reflux for 4 h with vigorous stirring, then worked up by cooling to room temperature and adding 30% H_2SO_4 (2 mL) in order to achieve good phase separation. The contents are transferred to a separatory funnel. The lower, aqueous layer is separated and filtered and solid sodium disulfite ($Na_2S_2O_5$) is added until the KI-starch test is negative (0.2–0.3 g). The aqueous layer is then basified to pH ≈ 8 (litmus) with solid Na_2CO_3 and evaporated to dryness at 50 °C (bath) under water-pump vacuum using a rotary evaporator. The residue is extracted (at 40 °C) by stirring with acetone (3 × 50 mL) and the extract is concentrated under reduced pressure to afford the crude diol **4** (9.4 g), which is dissolved in Et_2O (50 mL). This solution is passed through a short column (2.5 cm diameter) of silica gel (Merck, 70–230 mesh; 40 g), and Et_2O (650 mL) is then passed through the column to ensure complete elution of the product. Evaporation of the dried (Na_2SO_4) and filtered eluate gives diol **4b** as a nearly colorless oil; yield: 8.20 g (74%); purity: 98% (GLC); bp 83 °C/2 Torr (Lit.[21] 116 °C/11 Torr).

$C_3H_7ClO_2$	calc.	C 32.59	H 6.38	Cl 32.08
(110.5)	found	32.69	6.26	31.88

2,3-Dimethyl-2,3-butanediol (4j):

To a solution of H_2O_2 (**2**; 100 mmol) in H_2O (80 mL) (adjusted to pH 1.5 with 30% H_2SO_4) in a 250-mL round-bottomed flask equipped with stirrer, thermometer, and reflux condenser are added 2,3-dimethyl-2-butene (**1j**; 12.62 g, 150 mmol), benzene (10 mL), and methyltrioctylammonium tetrakis(diperoxotungsto)phosphate (**3a**; 0.902 g, 0.4 mmol). The resultant two-phase mixture is heated to reflux for 75 min with vigorous stirring, then worked up by adding 30% H_2SO_4 (4 mL) in order to achieve good phase separation. The warm mixture (containing a small amount of a heavy oily material, insoluble in both phases[30]) is transferred to a separatory funnel and the lower, aqueous layer is separated, filtered, neutralized with 30% NaOH, and then kept in an ice/water bath for 1 h, whereupon diol **4j** precipitates as the hexahydrate. The colorless crystalline product is isolated by suction and dried on a porous plate; yield: 16.43 g (72%); purity: 98% (GLC), 0.5–0.6% inorganic residue; mp 46–48 °C (H_2O) (Lit.[29] mp 46–47 °C).

$C_6H_{14}O_2 \cdot 6H_2O$	calc.	C 31.85	H 11.58
(226.3)	found	31.90	11.39

Note: In the initial stage, the reaction is in general quite exothermic. On operating at a larger scale (> 0.5 mol H_2O_2), thermal control is required.

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(1) Gunstone, F.D. *Adv. Org. Chem.* **1960**, *1*, 103.
(2) Swern, D., Billen, G.N., Findley, T.W., Scanlan, J.T. *J. Am. Chem. Soc.* **1945**, *67*, 1786.
Swern, D., Billen, G.N., Scanlan, J.T. *J. Am. Chem. Soc.* **1946**, *68*, 1504.
Käbisch, G., Malitius, H., Raupach, S., Trübe, R., Wittmann, H. *Eur. Patent Appl.* 25892, 25940 (1981); Degussa; *C.A.* **1981**, *95*, 80456, 80126.
(3) Criegee, R. *Liebigs Ann. Chem.* **1936**, *522*, 75.
Criegee, R., Marchand, E., Wannowius, H. *Liebigs Ann. Chem.* **1942**, 550, 99.
Hofman, K.A. *Ber. Dtsch. Chem. Ges.* **1912**, *45*, 3329.
Milas, N.A., Sussman, S. *J. Am. Chem. Soc.* **1936**, *58*, 1302; **1937**, *59*, 2345.
Sharpless, K.B., Akashi, K. *J. Am. Chem. Soc.* **1976**, *98*, 1986.
(4) Reisch, E., Zbiral, E. *Tetrahedron* **1979**, *35*, 1109.
Bhushan, V., Rathore, D.P., Chandrasekaran, S. *Synthesis* **1984**, 431.
(5) Mugdan, M., Young, D.P. *J. Chem. Soc.* **1949**, 2988.
(6) Hydroxylation of water-insoluble alkenoic acid derivatives in 50–80% yields has been reported. Preincorporation of ~ 2% of the glycol reaction product and preconditioning of the oxidizing system (70% H_2O_2 + tungstic acid) are required, however: Luong, T.M., Schriftman, H., Swern, D. *J. Am. Oil Chem. Soc.* **1967**, *44*, 316.
(7) Venturello, C., Alneri, E., Ricci, M. *J. Org. Chem.* **1983**, *48*, 3831.
(8) Venturello, C., Ricci, M. *J. Org. Chem.* **1986**, *51*, 1599.
(9) Venturello, C., D'Aloisio, R., Bart, J.C.J., Ricci, M. *J. Mol. Catal.* **1985**, *32*, 107.
(10) Venturello, C., D'Aloisio, R. *J. Org. Chem.* **1988**, *53*, 1553.
(11) Matoba, Y., Inoue, H., Akagi, J., Okabayashi, T., Ishii, Y., Ogawa, M. *Synth. Commun.* **1984**, *14*, 865.
(12) Ishii, Y., Yamawaki, K., Ura, T., Yamada, H., Yoshida, T., Ogawa, M. *J. Org. Chem.* **1988**, *53*, 3587.
(13) Schwegler, M., Floor, M., van Bekkum, H. *Tetrahedron Lett.* **1988**, *29*, 823.
(14) Wachi, T. *Japanese Patent* 7451233 (1974); *C.A.* **1974**, *81*, 120220.
(15) Käbisch, G., Malitius, H., Raupach, S., Trübe, R., Wittmann, H. *Ger. Offen.* 2755949 (1979), Degussa; *C.A.* **1979**, *91*, 56609.
(16) Kulka, K., Dittrick, J.W. *Cosmet. Perfum.* **1975**, 90, 90; *C.A.* **1975**, *83*, 65325.
(17) *Japanese Patent* 8104268 (1981), Shiseido Co., Ltd.; *C.A.* **1981**, *94*, 180491.
(18) Batog, A.E., Savenko, T.V., Batrak, T.A., Lomov, Y.M., Voloshkin, A.F. *USSR Patent* 922113 (1982); *C.A.* **1982**, *97*, 199089.
(19) Janssens, W., Heugebaert, F.C., Kokelenberg, H.E., *Ger. Offen.* 2719023 (1977), 2802666 (1978), Agfa-Gevaert; *C.A.* **1978**, *88*, 97428.
(20) Eliel, E.L., Freeman, J.P. *J. Am. Chem. Soc.* **1952**, *74*, 923.
(21) Böeseken, J., Hermans, P.H. *Recl. Trav. Chim. Pays-Bas* **1923**, *42*, 1106.
(22) Colonge, J., Cumet, L. *Bull. Soc. Chim. Fr.* **1947**, 840.
(23) Arpesella, L., La Manna, A., Grassi, M. *Gazz. Chim. Ital.* **1955**, *85*, 1364.
(24) Walti, A. *J. Am. Chem. Soc.* **1934**, *56*, 2725.
(25) Meiser, W. *Ber. Dtsch. Chem. Ges.* **1899**, *32*, 2050.
(26) Rigby, W. *J. Chem. Soc.* **1950**, 1911.
(27) Böeseken, J., Derkx, H.G. *Recl. Trav. Chim. Pays-Bas* **1921**, *40*, 530.
(28) Leuschner, G., Pfordte, K. *Liebigs Ann. Chem.* **1958**, *619*, 5.
(29) Toivonen, H. *Ann. Acad. Sci. Fenn., Ser. A2* **1956**, *Nr. 72*, 43; *C.A.* **1958**, *52*, 2806.
(30) The presence of such an oily to waxy material (from alteration of the catalyst) at the end of the reaction was observed in most cases with **3a**.